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Enthalpies of dilution of some electrolytes in water at 298.15 K

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Abstract

The enthalpies of dilution of Ph_4PCl, Ph_4AsCl, $NaPh_4B$ and R_4NBr (where R is ethyl, *n*-propyl, *n*-butyl and *n*-pentyl) have been determined by flow microcalorimetry at 298.15 K in water. From the experimental data, the relative apparent molar enthalpies ϕ_L were calculated with the aid of an extended Debye–Hückel equation. A comparison with literature values for some R_4NBr was made. Ph_4PCl and Ph_4AsCl show similar behavior, unlike that of $NaPh_4B$, which may be a consequence of the effect of the Na^+ ion in relation to the Cl^- ion.

INTRODUCTION

We are interested in the study of solute–solvent and solvent–solvent interactions in mixed aqueous solvents from various points of view, including the limiting molar partial volumes of electrolytes [1, 2] and the enthalpies of mixing [3]. In relation to the latter it is necessary, in a ternary system (electrolyte–non-electrolyte–water), to know the enthalpy of dilution of the electrolyte and non-electrolyte. Parker [4] and Fortier et al. [5] have studied the enthalpy of dilution of several electrolytes in water; however, for electrolytes such as *n*-Pen_4NBr, $NaPh_4B$, Ph_4PCl and Ph_4AsCl, values of the enthalpies of dilution in water have not been measured. The aim of this paper is to obtain values for the enthalpies of dilution of these electrolytes and of other R_4NBr electrolytes (where R is Et, *n*-Pr and *n*-Bu) which will be compared with literature values.

EXPERIMENTAL

Reagents

Sucrose (Merck for Biochemistry) was dried in vacuo overnight at room temperature. Urea (Merck, min 99.5%) was dried at 50°C in a vacuum

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desiccator. *N,N*-Diethylformamide (Aldrich, stated purity + 99%) (DEF) was used as received. Tetraalkylammonium bromides (Et_4NBr, *n*-Pr_4NBr, *n*-Bu_4NBr and *n*-Pen_4Br) from Fluka, of the best quality available, were purified as described by Conway et al. [6]. Their purity was checked by potentiometric titration against $AgNO_3$ previously standardized with NaCl. All R_4NBr had a purity greater than 99.7%. $Ph_4AsCl \cdot H_2O$ (Merck, min. 99%) was used as received. Ph_4PCl (Janssen Chimica, stated purity 99%) and $NaPh_4B$ (Merck, min. 99%) were dried at 80°C in a vacuum desiccator for three days. Water obtained from a Milli-Ro and Milli-Q water system (Millipore) ($\sigma \approx 10^{-4}$ S m^{-1}) was degassed prior to making up solutions by weight. All measurements were made with freshly prepared solutions.

Measurements of enthalpies of dilution

Enthalpies of dilution were measured with a Thermometric (TAM 2277) flow microcalorimeter at 298.15 ± 0.01 K. Details of this commercial microcalorimeter have been described by Suurkuusk and Wadsö [7]. The whole system was placed in a room in which the temperature was kept constant within ±0.5 K. A peristaltic pump with two channels (Gilson, Minipuls 3) or two HPLC pumps (Shimadzu LC-9A) were connected to the microcalorimeter. The flow rate of each pump was controlled after each dilution by weighing the liquids pumped. Several flux trials gave results reproducible within ±0.2% over a period of eight hours. It was observed that the stability of the output power was better with the peristaltic pump (0.04%) than with the HPLC pumps (0.2%), but the results with both pumps fall within the experimental accuracy. The total flow rate was approx. 0.48 cm^3 min^{-1} in the peristaltic pump, and 0.60 cm^3 min^{-1} for the HPLC pumps.

The molar enthalpy of dilution was obtained from the expression

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = (W - W_0)\frac{f}{m_{\mathrm{f}}F} \tag{1}$$

where W and W_0 are the thermal effects expressed as power in watts corresponding to a dilution experiment and the baseline produced by two identical liquids, respectively, f is a correction factor for heat losses, m_{f} is the final concentration in mol kg^{-1} and F is the flow rate of water expressed in kg s^{-1} at the outlet of the microcalorimeter. The microcalorimeter was calibrated electrically for each enthalpy of dilution measurement. The uncertainty in the enthalpy of dilution was $< \pm 1\%$. Nevertheless, in order to check the accuracy of our system, measurements of the enthalpy of dilution of sucrose, urea and DEF were performed. The results of the molar enthalpies of dilution from some initial composition m_{i} to a final solution m_{f}, $\Delta_{\mathrm{dil}}H_{\mathrm{m}}(m_{\mathrm{i}} \rightarrow m_{\mathrm{f}})$, are normally expressed in terms of relative apparent molar enthalpies ϕ_{L}, according to the equation

$$\phi_{\mathrm{L}} = A_1 m + A_2 m^2 + A_3 m^3 + \ldots \tag{2}$$

TABLE 1

Values of coefficients for eqn. (2) and standard deviation s of the fit [a]

Non-electrolyte	$A_1/(\mathrm{J\ kg\ mol^{-2}})$	$A_2/(\mathrm{J\ kg\ mol^{-3}})$	$s/(\mathrm{J\ mol^{-1}})$	Molality range
Sucrose	570.3 (15)	−52.3 (13)	3	$\leqslant 1.05$
Urea	−353.4 (7)	19.7 (4)	2	$\leqslant 1.50$
DEF	1823.5 (40)	−112.1 (17)	11	$\leqslant 1.92$

[a] Numbers in parentheses are the 95% confidence limits.

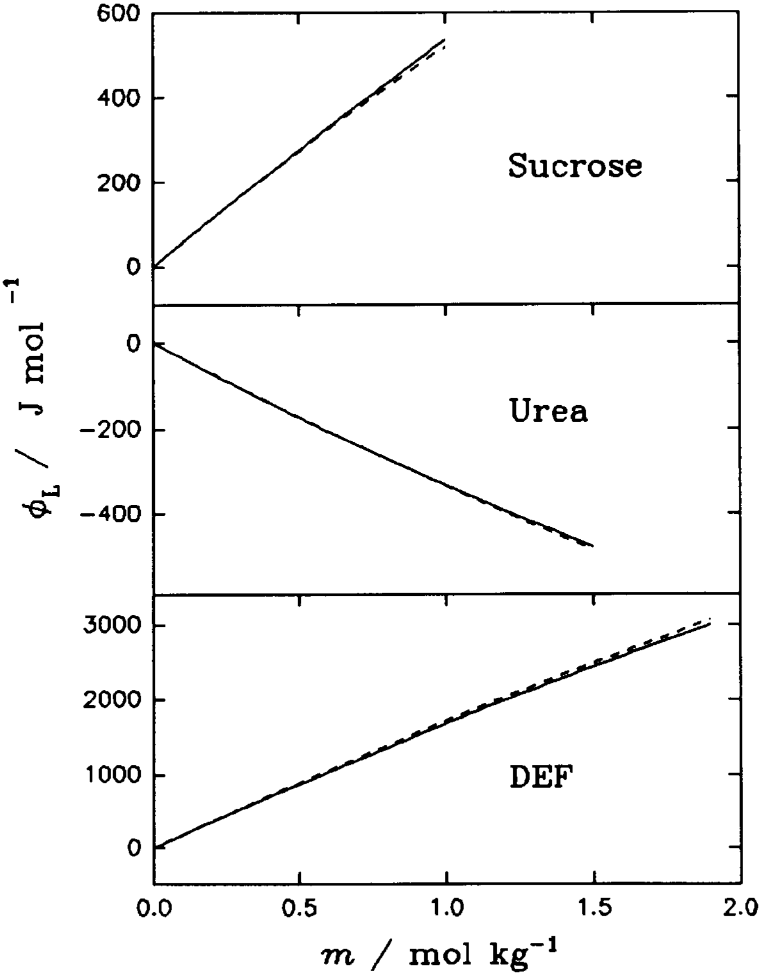

Fig. 1. Plot of ϕ_L against molal concentration for sucrose (——, this work; – – –, ref. 8); urea (——, this work; – – –, ref. 8); DEF (——, this work; – – –, ref. 9).

where m is the concentration in mol kg^{-1} and the coefficients A_j ($j = 1, 2, \ldots$) are given in Table 1. A comparison with the literature values made in Fig. 1 shows that the agreement was good.

RESULTS AND DISCUSSION

The experimental values of the enthalpies of dilution for the electrolytes studied, $\Delta_{\mathrm{dil}}H_{\mathrm{m}}(m_{\mathrm{i}} \rightarrow m_{\mathrm{f}})$, are given in Table 2. The enthalpy of dilution can be expressed in terms of the relative apparent molar enthalpy ϕ_{L} by the equation

$$\Delta_{\mathrm{dil}}H = \phi_{\mathrm{L}}(m_{\mathrm{f}}) - \phi_{\mathrm{L}}(m_{\mathrm{i}}) \tag{3}$$

TABLE 2

Enthalpies of dilution for various electrolytes in water at 298.15 K

m_{i}/(kg mol^{-1})	m_{f}/(kg mol^{-1})	$\Delta_{\mathrm{dil}}H$/(J mol^{-1})	δ ^{a}/(J mol^{-1})
Ph_4AsCl			
0.01821	0.00708	−510.3	−15.5
0.01821	0.00928	−367.2	18.8
0.01821	0.01186	−269.0	−2.5
0.02695	0.01046	−657.9	−7.7
0.02695	0.01372	−496.7	7.8
0.02695	0.01754	−345.5	0.6
0.03896	0.01507	−828.8	−9.9
0.03896	0.01979	−626.0	4.2
0.03896	0.02532	−426.7	1.4
0.06830	0.02627	−1040.6	22.9
0.06830	0.03453	−807.1	−9.6
0.06830	0.04425	−544.0	−19.3
$NaPh_4B$			
0.04940	0.01432	−679.1	0.7
0.04940	0.02535	−435.7	14.0
0.04940	0.03491	−263.8	1.3
0.08290	0.02388	−1056.9	−4.9
0.08290	0.04230	−696.0	4.9
0.08290	0.04236	−688.9	10.8
0.11680	0.03423	−1393.9	1.9
0.11690	0.05938	−930.2	14.0
0.11680	0.08209	−551.3	7.3
0.14950	0.04251	−1779.0	−32.4
0.14950	0.07561	−1165.0	5.8
0.14950	0.10480	−669.7	24.6
Ph_4PCl			
0.01961	0.00570	−565.7	−1.9
0.01961	0.01001	−356.4	9.9
0.01961	0.01385	−209.7	0.4
0.02786	0.00808	−717.5	−2.1
0.02786	0.01420	−454.2	6.7
0.02786	0.01966	−271.7	−9.2
0.05110	0.01812	−910.8	−3.4
0.05110	0.02614	−634.7	8.5
0.05110	0.03261	−459.9	−5.9

TABLE 2 (continued)

$m_i/(\mathrm{kg\,mol^{-1}})$	$m_f/(\mathrm{kg\,mol^{-1}})$	$\Delta_{\mathrm{dil}}H/(\mathrm{J\,mol^{-1}})$	δ [a]$/(\mathrm{J\,mol^{-1}})$
0.09729	0.03419	−1197.9	−9.0
0.09729	0.04942	−800.4	14.6
0.09729	0.06178	−564.1	−3.5
0.14970	0.05207	−1291.2	−4.6
0.14970	0.07546	−835.9	11.9
0.14970	0.09452	−574.6	−8.8
Et_4NBr			
0.09680	0.03472	291.9	8.7
0.09680	0.04941	219.6	1.5
0.09680	0.06085	166.0	0.5
0.14900	0.05316	427.9	3.7
0.14900	0.07573	318.2	−1.5
0.14900	0.09333	238.7	−0.2
0.19160	0.06801	505.7	−11.2
0.19160	0.09702	384.2	0.6
0.19160	0.11971	287.2	3.7
0.22080	0.07815	557.9	−11.1
0.22080	0.11155	424.1	6.0
0.22080	0.13770	319.9	13.4
n-Pr_4NBr			
0.07902	0.02638	138.3	22.0
0.07902	0.03990	99.2	10.6
0.07902	0.05198	62.3	1.4
0.11820	0.03923	131.1	−32.8
0.11820	0.05941	119.7	2.1
0.11820	0.07750	75.4	−1.7
0.14750	0.04873	186.2	3.5
0.14750	0.07389	122.1	−3.3
0.14750	0.09649	72.4	−6.4
0.19790	0.06488	190.4	6.7
0.19790	0.09858	116.1	3.1
0.19790	0.12895	61.7	−0.6
n-Bu_4NBr			
0.08112	0.02859	−249.3	0.5
0.08112	0.04125	−194.7	3.6
0.08112	0.05164	−153.0	−0.9
0.09520	0.03346	−313.5	−0.6
0.09520	0.04831	−245.0	4.7
0.09520	0.06051	−191.9	−0.1
0.12130	0.04243	−446.1	−4.4
0.12130	0.06133	−349.2	4.5
0.12130	0.07688	−273.1	−1.1
0.15990	0.05553	−661.0	−8.7
0.15990	0.08041	−513.0	9.5
0.15990	0.10094	−401.9	−0.8

TABLE 2 (continued)

m_i/(kg mol^{-1})	m_f/(kg mol^{-1})	$\Delta_{dil}H$/(J mol^{-1})	δ [a]/(J mol^{-1})
n-Pen$_4$NBr			
0.01944	0.00741	−172.3	−16.7
0.04347	0.01434	−464.6	6.7
0.04347	0.01537	−453.9	5.4
0.04347	0.01651	−445.1	1.0
0.04347	0.01792	−427.5	2.4
0.04347	0.01955	−404.8	5.9
0.04347	0.02156	−377.6	8.7
0.04347	0.02398	−340.8	14.3
0.04347	0.02701	−293.9	19.0
0.04347	0.03102	−227.4	22.7
0.07457	0.02809	−1264.3	−35.7
0.07457	0.03051	−1216.7	−26.2
0.07457	0.03332	−1158.1	−15.9
0.07457	0.03670	−1080.4	−2.1
0.07457	0.04085	−980.7	10.8
0.07457	0.04606	−846.4	23.0
0.07457	0.05297	−658.7	27.6
0.15520	0.07561	−1653.8	69.5
0.15520	0.08425	−1493.6	−70.9

[a] Difference between experimental value and those calculated by eqn. (5).

TABLE 3

Values of coefficients for eqn. (5) and standard deviations s of the fit [a]

Electrolyte	B_L/ (J kg mol^{-2})	C_L/ (J kg$^{3/2}$ mol$^{-5/2}$)	D_L/ (J kg^2 mol^{-3})	E_L/ (J kg$^{5/2}$ mol$^{-7/2}$)	s/ (J mol^{-1})
Ph$_4$AsCl	51302 (2289)	−94799 (7585)			14
NaPh$_4$B	14447 (1187)	−3160 (2723)			15
Ph$_4$PCl	48958 (2170)	−118221 (11680)	83080 (16830)		9
Et$_4$NBr	−12281 (478)	9860 (868)			8
n-Pr$_4$NBr	−10905 (846)	12472 (1671)			13
n-Bu$_4$NBr	−10640 (3779)	40424 (17330)	−27435 (21730)		5
n-Pen$_4$NBr	59371 (47160)	−735634 (422200)	3309588 (1349000)	−4338750 (1452000)	32

[a] Numbers in parentheses are the 95% confidence limits.

where ϕ_L can be expressed as a function of the electrolyte concentration as

$$\phi_L = A_L m^{1/2} + B_L m + C_L m^{3/2} + D_L m^2 + \ldots \tag{4}$$

where $A_L = 1972$ J kg$^{1/2}$ mol$^{3/2}$ is the limiting Debye–Hückel slope at 298.15 K, and B_L, C_L, etc., are curve-fitting parameters which are related to the solute–solute interactions. Equations (3) and (4) can be combined in the form

$$\Delta_{\mathrm{dil}}H - A_L(m_f^{1/2} - m_i^{1/2}) = B_L(m_f - m_i) + C_L(m_f^{3/2} - m_i^{3/2}) + D_L(m_f^2 - m_i^2) + \ldots \tag{5}$$

where B_L, C_L, D_L, etc., were obtained using a least-squared analysis. The number of parameters was chosen so that were significant with respect to

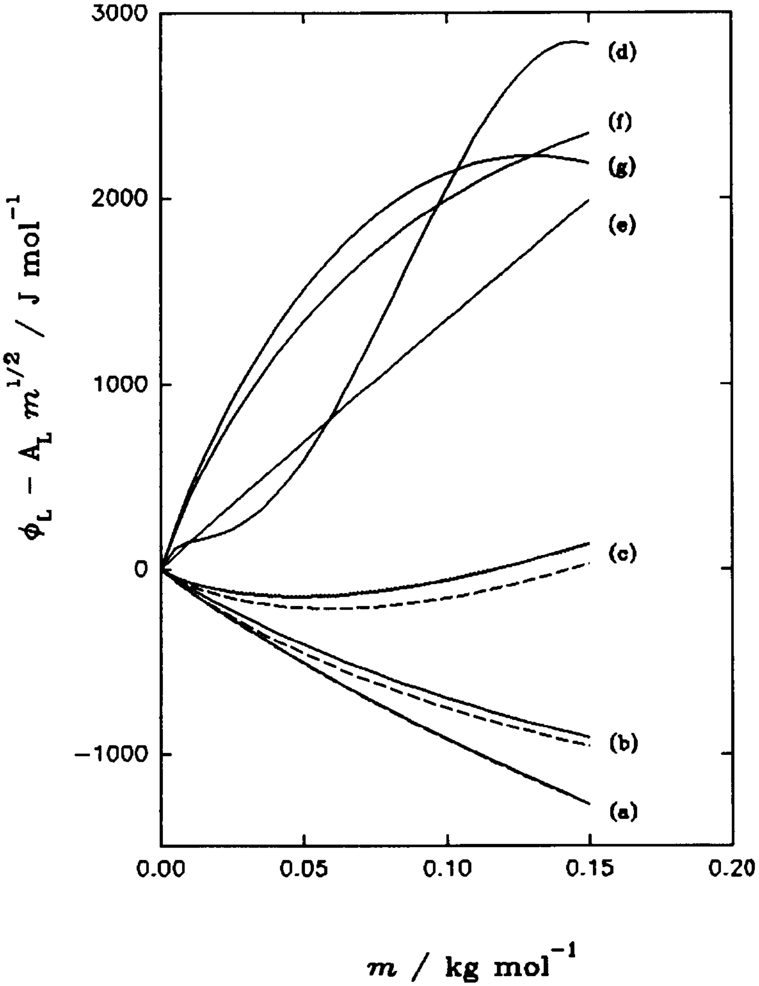

Fig. 2. Plot of $\phi_L - A_L m^{1/2}$ against molal concentration for (a) ≡Et$_4$NBr (——, this work; – – –, ref. 10); (b) ≡n-Pr$_4$NBr (——, this work; – – –, ref. 10); (c) ≡n-Bu$_4$NBr (——, this work; – – –, ref. 10; · · ·, ref. 11); (d) ≡n-Pen$_4$NBr; (e) ≡NaPh$_4$B; (f) ≡Ph$_4$PCl; (g) ≡Ph$_4$AsCl.

their uncertainties (95% confidence limits). In Table 3 the coefficients of eqn. (5) are reported, and in Fig. 2 we have plotted $\phi_L - A_L m^{1/2}$ against m, where for R_4NBr we have also included values from other authors. For Et_4NBr and n-Pr_4NB, the accordance with the values of Levine and Wood [10] is satisfactory, but with n-Bu_4NBr our results are in better agreement with those of Fortier et al. [11] than with those in ref. 10. The upper part of Fig. 2 shows that the behavior of Ph_4PCl is quite similar to that of Ph_4AsCl, a consequence of their nearly equal size, and equal charge and counter-ion. The variation of $\phi_L - A_L m^{1/2}$ with m for $NaPh_4B$ is nearly linear, which may be a consequence of the counter-ion Na^+ in relation to Cl^- ion, because the dimensions of both Ph_4P^+ or Ph_4As^+ and Ph_4B^- are comparable. However, in the case of tetraalkylammonium halides, the values of ϕ_L are chiefly dependent on the R_4N^+ ion [12].

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